



Waste Treatment Plant Project

The Waste Treatment Plant Leaching Process

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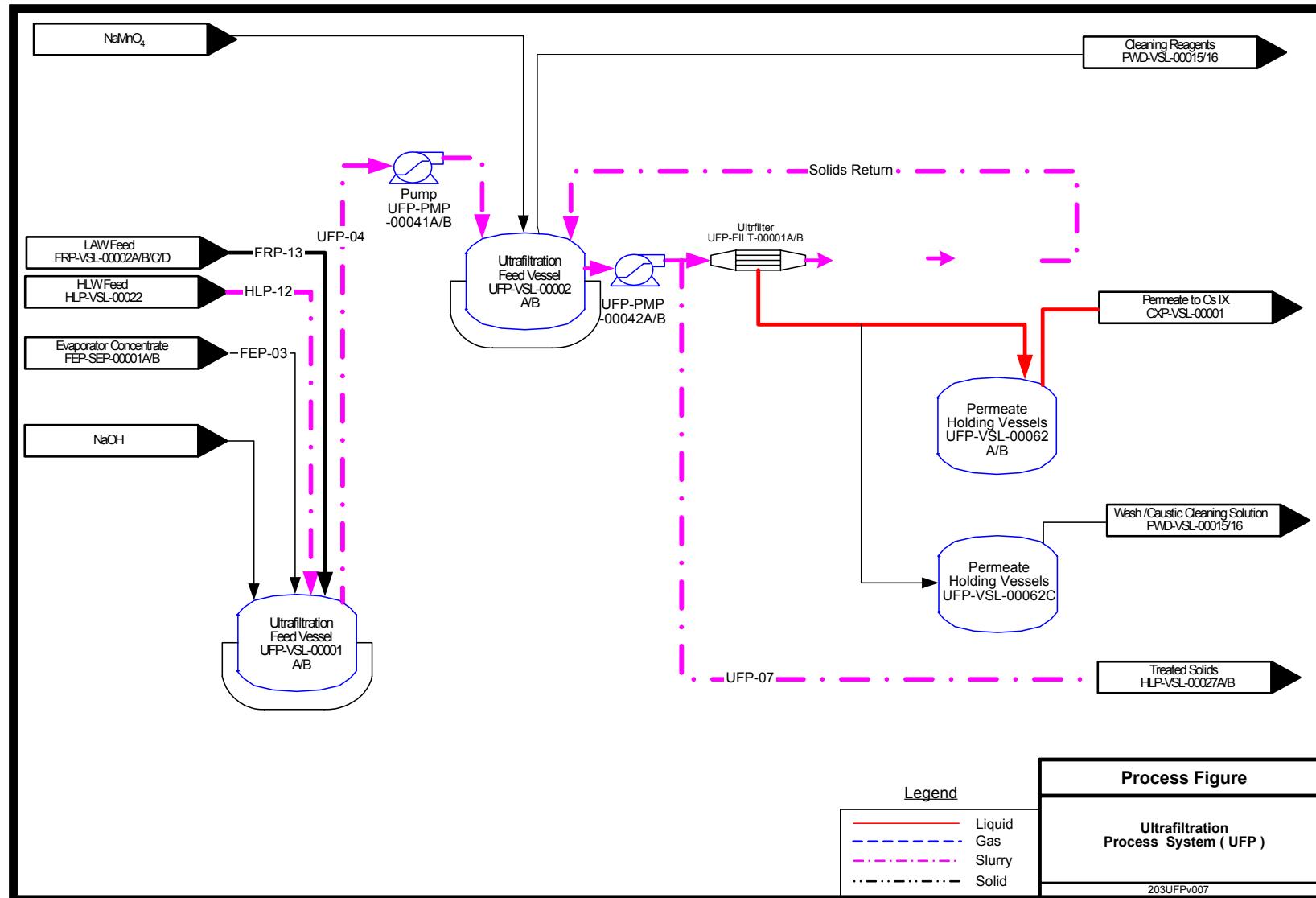
Introduction

- WTP Ultrafiltration System Overview
- Process Assumptions
- Chemical Modeling and Aluminum Solubility
- Recent Modifications
- Research and Technology Program, Bench and Large Scale
- Follow on Work

Leaching Process

- The Waste Treatment Plant uses caustic leaching (NaOH) to dissolve aluminum and oxidative leaching (NaMnO_4) to dissolve chromium from sludge.
- Aluminum and chromium are removed from the sludge to minimize the mass of High-Level Waste (HLW) glass made.
- The leaching process occurs within the Ultrafiltration System in the plant.
- The Ultrafiltration system is a batch process.

Ultrafiltration Process Figure



Ultrafiltration Process Description

- Receive HLW and Low-activity waste (LAW) feed into UFP01 Vessels.
- For aluminum removal from sludge, add 19 M NaOH and heat to 100 °C for ~ 8 hours (~36 hour cycle for heat, digest, and cooling). Cool back down to 25-45 °C.
- Transfer to UFP02 Vessels.
- Remove leachate by ultrafiltration, target concentration of 20 Wt-% solids.

Ultrafiltration Process Description

- Filter permeate is transferred to Vessels UFP62A,B, in route to the Ion-Exchange System.
- Sludge in UFP02 Vessels is washed until the free hydroxide is <0.25 M.
- NaMnO_4 is added to sludge to dissolve Cr(III) by oxidation.
- Quantity of NaMnO_4 is between 1 and 1.25 moles of Mn per mole of Cr(III).

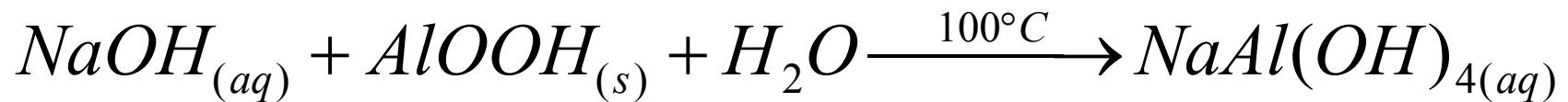
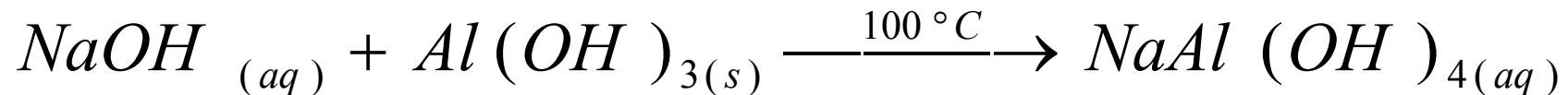
Ultrafiltration Process Description

- Sludge is water washed to remove Cr(VI) soluble product and re-concentrated back to ~20 Wt-% solids.
- Oxidative leach permeate is recycled back to the FEP evaporator for concentration, and becomes part of the supernatant for later UFP system batches.
- Washed solids are transferred to the HLP (HLW Lag Storage) System.

Forms of Aluminum in Waste

- Al(OH)_3 , Gibbsite and Bayerite have same chemical formula, gibbsite more common.
- AlOOH , Boehmite and Psuedoboehmite. Psuedoboehmite is just boehmite that is very small and because of its high surface area, is much less stable than regular Boehmite.
- $\text{Na}_3\text{Al}(\text{CO}_3)_2$, Dawsonite. Found in high-carbonate feeds (hot commissioning feed).
- Amorphous Aluminum Hydroxide. Short lived, usually formed from rapid precipitation of aluminum.
- Many Aluminosilicates. They do not dissolve rapidly in caustic.
- Gibbsite and Boehmite are most prevalent.

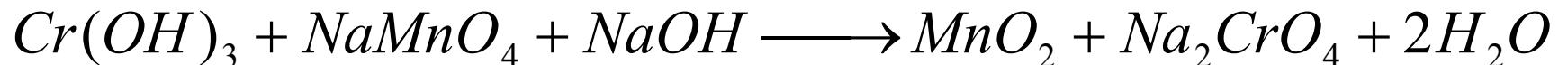
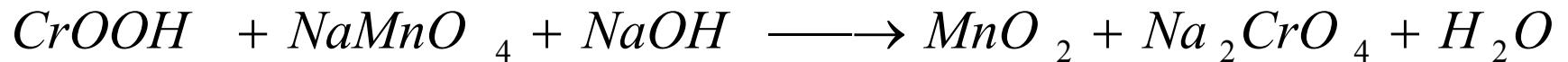
Caustic Leaching Reactions



Forms of Cr(III) in Waste

- CrOOH
- X-Ray amorphous phases, probably Cr(OH)_3
- Many mixed-metal phases
- Cr-containing Spinels

Oxidative Leaching Reactions



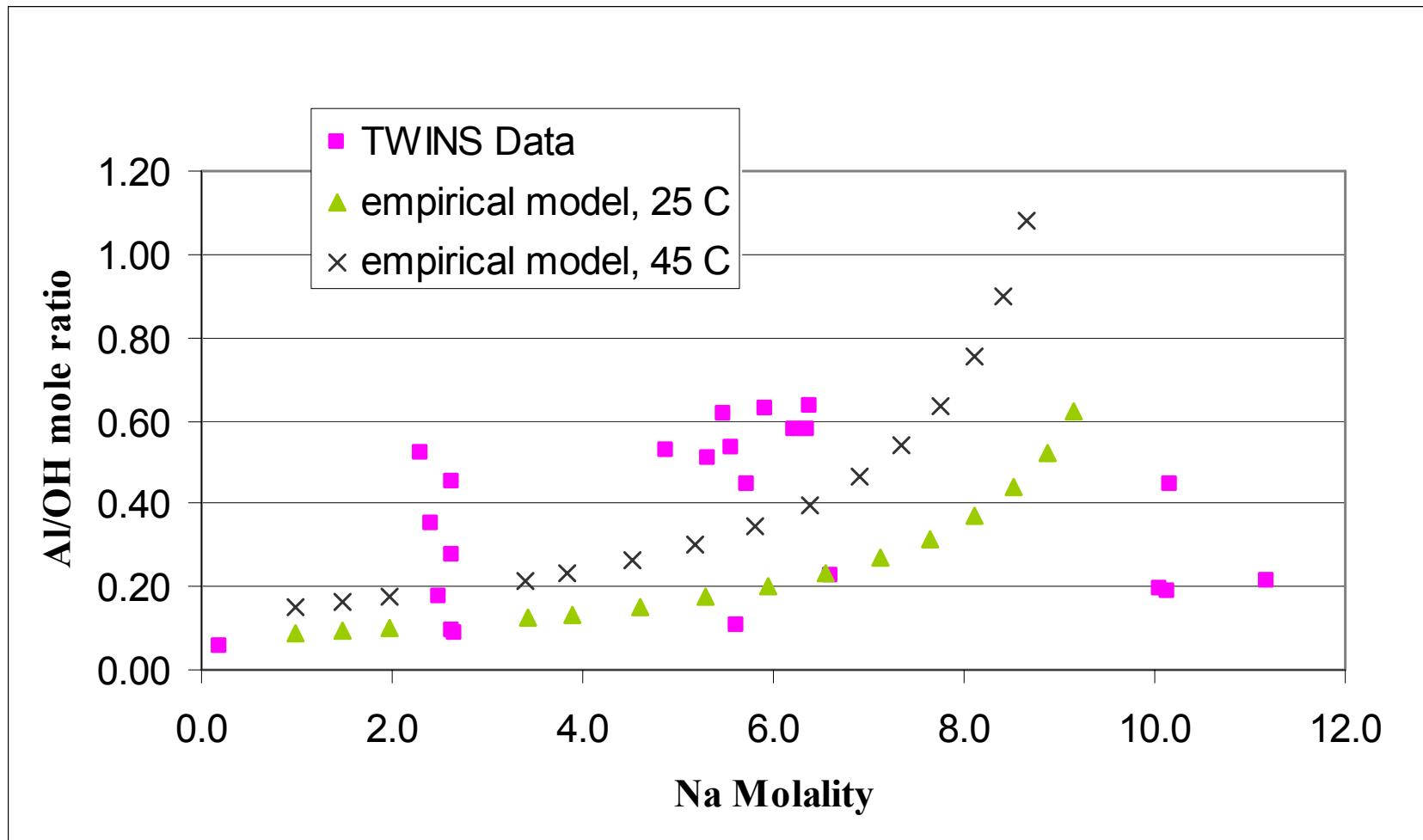
Aluminum Leaching Modeling Assumptions

- The aluminum solubility relationships in dynamic model provide conservative estimates of required caustic.
- Specified processing times are long enough to approach equilibrium.
- Aluminum supersaturation is avoided during leaching, cooling and washing by caustic addition.
- TFC provides leach factors for aluminum along with the feed vector. We assume that these are the best available information on the quantity of aluminum leachable under our conditions.

Aluminum Solubility Modeling

- We use two models, depending on the application.
- Thermodynamic model (ESP, by OLI Inc.) for rigorous evaluations.
- We use an empirical model that assumes that aluminum solubility in waste is the same as in an equivalent strength of sodium hydroxide.
- The empirical model is conservative because the electrolytes in waste increase the solubility over pure hydroxide solutions.
- The empirical model is used when conservatism is needed, such as tank utilization and throughput evolutions.

Comparison of Empirical Model to Tank Data



Model Predictions of Solubility

- Current flowsheets assume that the quantity of hydroxide needed during leaching is the quantity needed to keep the aluminum soluble at 45 °C after leaching. Additional NaOH can be added downstream of filter to prevent aluminum from precipitating at 25 °C.
- Empirical model conservatively predicts the quantity of caustic needed to keep aluminum soluble after leaching for most feeds.
- The thermodynamic model also conservatively predicts aluminum solubility for many feeds, but this is believed (but not confirmed) to be because of slow aluminum precipitation kinetics.

Why has the NaOH Quantity Used in Leaching Increased?

- Older flowsheets did not remove all of the leachable aluminum.
- Older models under-predicted hydroxide needed for the feeds with the highest aluminum concentration, which is why we switched to a more conservative model.
- Most of the increase in NaOH usage is because we now add enough NaOH to alleviate the supersaturation of the feed. The majority of the feeds in the feed vector are supersaturated with gibbsite, and gibbsite would precipitate if additional NaOH were not added.

Caustic Addition and Kinetics

- Current caustic addition in the flowsheet is based on thermodynamic considerations.
- The sodium hydroxide concentration is known to impact aluminum dissolution kinetics.
- The current caustic addition method is being evaluated against kinetic requirements.

Chromium Leaching Modeling Assumptions

- Permanganate is added at a 1.1:1 mole ratio to Cr.
- The free hydroxide concentration needs to be below 0.25 M to minimize Pu oxidization by the permanganate.
- At least 86% of the Cr(III) is removed and only trace amounts of Pu are mobilized under these conditions.
- These assumptions are currently being tested by the R&T program.

What Are We Doing in the Ultrafiltration Area of Flowsheet?

- Changes Driven by External Flowsheet review Team (EFRT)
- Design Changes
- Lab Scale R&T Work
- Large-Scale R&T work
- Reconcile Results with the Flowsheets
- Follow-on R&T Work
- Risk Mitigation

Pretreatment Design Modifications

- PT 1- Increase Effective Ultrafilter Area
- PT 2- In-line Reagent Mixing (model unchanged)
- PT 3- Upfront Caustic Leaching (UFP-01 rather than UFP-02)
- PT 4- Caustic Leaching at 100°C
- PT 5- UFP02A/B Heel Transferred Forward
- PT 6- Ultrafilter and Oxidative Leach at 45°C
- PT 7- Caustic addition for leaching in UFP-02A/B based on aluminate solubility at 45°C, remaining caustic needed for 25°C added in UFP62A/B
- PT 8- Increased ion exchange capacity to 30 GPM instantaneous rate, 22 GPM nominal

Lab Scale R&T Work

- Perform real-waste leaching studies to identify appropriate simulants for Gibbsite, Boehmite, and Cr-containing solids.
- Perform screening tests to determine significant factors affecting dissolution kinetics.
- Develop method to determine appropriate quantity of permanganate that maximizes Cr dissolution but minimizes Pu dissolution.
- Develop simulant for large scale testing.
- Validate filter flux equations against real waste.

Large Scale Testing

- The Pretreatment Engineering Platform (PEP).
- Scale = $1/(4.5^3)$ of full WTP.
- Primarily will develop scaling factors (dissolution rates & filter flux) for adjusting bench scale test results to $\frac{1}{4}$ scale UFP.
- Validate that design modifications were effective.
- Evaluate process control strategy.

Process Risks

- Treated solids concentration could be below 20-wt% target for some feeds.
- Post-filtration precipitation from temperature change, slow precipitation kinetics in ultrafilter, aluminosilicates, and blending of streams downstream of filter.
- Salt (sodium oxalate and other salts) fly-wheeling in the recycle system
- Slow aluminum dissolution kinetics
- Pu mobilization

Follow on Work and Testing

- Risk mitigation testing.
- Sufficient Boehmite and Gibbsite dissolution rate data for full Helgeson dissolution Rate Law.
- Large scale testing with wider range of simulants to test robustness of process.
- Develop procedure for determining feed-specific quantity of NaOH and NaMnO₄ addition.
- Control strategy maturation.

Conclusions

- The Waste Treatment Plant uses caustic leaching to remove aluminum and oxidative leaching to remove chromium.
- Considerable improvements have been made in the plant design to optimize UFP system performance.
- A research program has been developed to test assumptions and mitigate risks.
- Both thermodynamic and empirical models have been employed to conservatively and rigorously model the leaching process.